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Research Article

## An efficient and facile synthesis of the hybrid scaffold of Pyrazole-Triazole-Chromenes nucleus using PS-TBD as a green catalyst

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### ABSTRACT

A series of 16 derivatives of pyrazole-triazole-chromene moieties (4a-p) were synthesized via one-pot cyclocondensation reaction of pyrazole-triazole aldehyde (1a-d), 1, 3 diketone (3a-d) and malononitrile (2a) in presence of PS-TBD as catalyst. The reusability of PS-TBD (polystyrene supported 7-methyl-1, 5, 7-triazabicyclo [4.4.0] dec-5-ene) catalyst makes this reaction quick and efficient. On the basis of various trials and its results, best performance and reusability of catalyst was observed at 5 mol% concentration. The reusability of catalyst founds up to 5 runs. A synthesized compound was characterized by <sup>1</sup>HNMR, <sup>13</sup>CNMR, FT-IR and C, H, N elemental analysis and confirms theoretical chemical reaction.

**Keywords:** Chromenes, Pyrazole, Triazole, PS-TBD catalysis Chemistry

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## 1. INTRODUCTION

Polymer-supported catalysts have an appeal much attention in recent decades due to their inherent advantages in green chemistry, for example, simplification of reaction procedures including the easy recovery of the catalyst by filtration, application to automated systems, and recycling of catalyst. In any polymer supported catalyst catalyzed a reaction, after the completion of reaction catalyst can be easily collected and reused catalyst.<sup>[1-4]</sup> Green chemistry emphasizes the development of environmentally benign chemical processes and technologies. So it will be equally beneficial for the environment as well as for the cost of green chemistry.<sup>[5]</sup> The Much Vantage of catalyst PS-TBD are reusability, cleanness and less harmful to the environment, makes the chemical reaction more eco-friendly, economic and environmental advantages.<sup>[6]</sup> The PS-TBD is a polymer-supported organocatalyst consisting of a covalently linked guanidine TBD moiety to polystyrene which has been successfully used in a wide range of reactions, as epoxide ring opening, aldol-type condensation<sup>[7]</sup>, Knoevenagel condensation<sup>[7]</sup>, Michael additions<sup>[7]</sup> to  $\alpha$ ,  $\beta$ -unsaturated ketones, cyanosilylation of aldehydes, ketones, and imines<sup>[7]</sup>, ring opening of aziridines and addition of dialkylphosphites to unsaturated systems. This series novel compounds softwood with polystyrene supported 7-methyl-1, 5, 7-triazabicyclo [4.4.0] dec-5-ene (PS-TBD).pyrano[4, 3-b]pyran and pyrano[3, 2-c]chromene compounds. In the continuation of our previous work we use PS-TBD (polystyrene supported

7-methyl-1, 5, 7-triazabicyclo[4.4.0]dec-5-ene) a catalyst for the one pot cyclocondensation reaction of triazole-pyrazole substituted aldehyde, various active methylene compounds, and malononitrile<sup>[8-12]</sup>. All synthesized compounds were characterized by various physicochemical methods.

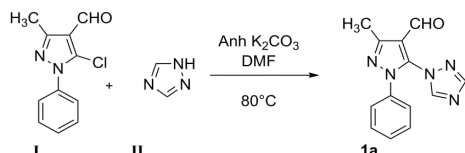
## 2. EXPERIMENTAL

All the reagents and solvents were obtained commercially and used without further purification. All melting points were taken in open capillaries and are uncorrected. For monitoring the progress of all reactions and purity of the synthesized compounds thin-layer chromatography (TLC, on aluminium plates precoated with silica gel 60F254, Merck, Darmstadt, Germany) was used; eluent hexane: ethylacetate (1:1). UV radiation and/or iodine were used as the visualizing agents. The IR spectra were recorded Perkin-Elmer Spectrum GX FT-IR Spectrophotometer (Perkin-Elmer, USA), only the characteristic peaks are reported in  $\text{cm}^{-1}$ . Elemental analysis (% C, H, N) was carried out by Perkin-Elmer 2400 series-II elemental analyzer (Perkin-Elmer, USA); all compounds are within  $\pm 0.4\%$  of theory specified. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a BrukerAvance 400F (MHz) spectrometer (Bruker Scientific Corporation Ltd., Switzerland) using solvent peak as internal standard at 400 MHz and 100 MHz respectively. Chemical shifts are reported in parts per million (ppm). Mass spectra were scanned on a Shimadzu LCMS 2010 spectrometer (Shimadzu, Tokyo, Japan).

## 2.1. General procedure for the synthesis of targeted compounds

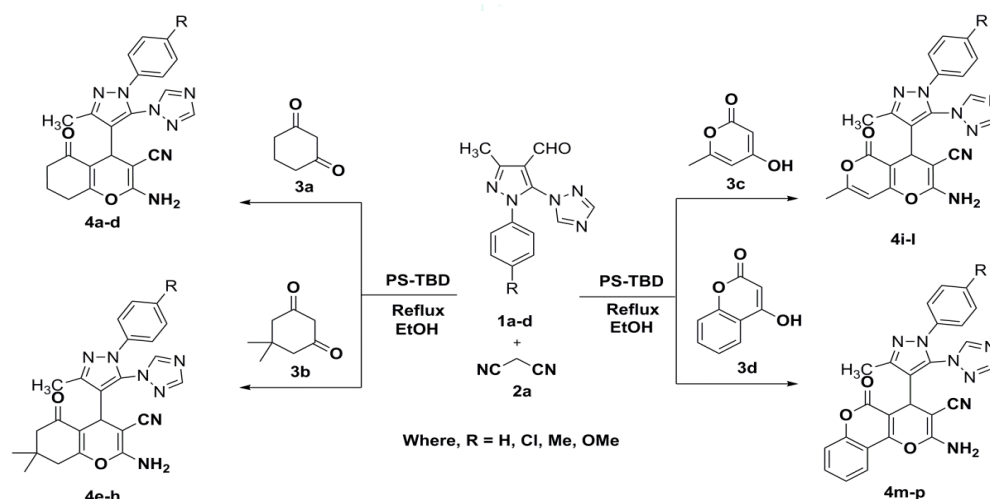
### 2.1.1. Synthesis of 3-methyl-1-(4-substituted phenyl)-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazole-4-carbaldehyde

Triazole substituted aldehyde (1a-d) was synthesized by heating previously prepared 0.05 mole substituted 5-chloro-3-methyl-1-(4-substituted phenyl)-1H-pyrazole-4-carbaldehyde [13-15] (**I**) and 0.05 mole 1H-1, 2, 4-triazole (**II**) and 0.075 mole of anhydrous Potassium carbonate ( $K_2CO_3$ ) in dimethyl formamide at 80°C for 2 hr. After the completion of reaction monitoring by TLC, the reaction mass was poured into crushed ice. The product obtained was filtered, washed, dried and recrystallized from ethyl acetate.



Scheme 1: Synthesis of 3-methyl-1-phenyl-5-(1H-1,2,4-triazol-1-yl)-1H-pyrazole-4-carbaldehyde

[Scheme 1]



[Scheme 2]

Table 1: Optimization of reaction condition for 4a

Entry	Temperature (C)	Time (h)	Mol % PS-TBD	%Yield <sup>a</sup>
1	RT	2	-	56
2	60	2	2	72
3	80	2	2	75
4	80	1.5	5	88
5	80	1.5	8	~88

<sup>a</sup> Isolated yield

3- Phenyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazole-4-carbaldehyde **1a** (5 mmol), malononitrile **2** (5 mmol) and 4-hydroxy coumarin **6** (5 mmol)

Table 2: Activity of reused catalyst for synthesis of 4a

Run	%Yield <sup>a</sup>
1 <sup>st</sup>	88
2 <sup>nd</sup>	85
3 <sup>rd</sup>	81
4 <sup>th</sup>	76
5 <sup>th</sup>	73

<sup>a</sup> Isolated yield

2-amino-4-(3-methyl-1-phenyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (**4a**)

White solid (1.689 g, 96%), mp 223°C; IR (KBr):  $\nu$  = 3428, 3344, 2189, 1677, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.93 (3H) 1.94–2.92 (6H, m,  $3\times\text{CH}_2$ ), 4.23 (1H, s,  $\text{H}_4$ ), 7.58–8.54 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.84 (2H, s, NH) ppm; MS calcd. for  $\text{C}_{22}\text{H}_{19}\text{N}_7\text{O}_2$   $[\text{M}]^+$  413.16, found 413.44; Anal. calcd. C, 63.91; H, 4.63; N, 23.72; O, 7.74; Found: C, 64.19; H, 4.43; N, 23.40; O, 7.59 %  $^{13}\text{C}$  NMR, 13.1, 21.3, 28.2, 29.0, 36.6, 58.3, 112.4, 118.9, 119.3, 199.4, 119.5, 125.7, 129.5, 129.9, 139.7, 147.5, 151.3, 152.4, 154.3, 155.4, 159.5, 198.2.

2-amino-4-(1-(4-chlorophenyl)-3-methyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4b)

White solid (1.729 g, 96%), mp 225 °C; IR (KBr):  $\nu$  = 3416, 3356, 2195, 1673, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.92 (3H), 1.93–2.93 (6H, m,  $3\times\text{CH}_2$ ), 4.23 (1H, s,  $\text{H}_4$ ), 7.58–8.26 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.84 (2H, s, NH) ppm; MS calcd. for  $\text{C}_{22}\text{H}_{18}\text{ClN}_7\text{O}_2$   $[\text{M}]^+$  447.12, found 447.88; Anal. calcd. C, 59.00; H, 4.05; Cl, 7.92; N, 21.89; O, 7.14; Found: C, 59.31; H, 4.17; Cl 7.52; N, 21.95; O, 6.93%;  $^{13}\text{C}$  NMR 12.9, 21.5, 28.5, 28.9, 36.9, 58.4, 113.0, 118.0, 118.2, 118.5, 118.8, 129.6, 130.3, 131.6, 137.9, 147.5, 151.5, 152.7, 154.6, 155.0, 158.2, 197.5.

2-amino-4-(3-methyl-1-(p-tolyl)-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4c)

White solid (1.619 g, 95%), mp 224 °C; IR (KBr):  $\nu$  = 3399, 3365, 2195, 1673, 1255  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.94 (3H), 1.94–2.92 (6H, m,  $3\times\text{CH}_2$ ), 4.32 (1H, s,  $\text{H}_4$ ), 7.25–7.51 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.80 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{23}\text{H}_{21}\text{N}_7\text{O}_2$   $[\text{M}]^+$  427.18, found 427.47; Anal. calcd. C, 64.63; H, 4.95; N, 22.94; O, 7.49; Found: C, 64.39; H, 5.13; N, 22.61; O, 7.12%  $^{13}\text{C}$  NMR, 13.0, 21.6, 21.6, 28.6, 28.6, 36.7, 57.5, 113.2, 119.2, 119.6, 125.2, 125.5, 129.0, 129.1, 135.8, 136.9, 146.2, 151.3, 152.4, 154.1, 155.3, 159.4, 197.8.

2-amino-4-(1-(4-methoxyphenyl)-3-methyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4d)

White solid (1.889 g, 96%), mp 224 °C; IR (KBr):  $\nu$  = 3374, 3295, 2208, 1677, 1275  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = (3H), 1.92–2.89 (6H, m,  $3\times\text{CH}_2$ ), 4.11 (1H, s,  $\text{H}_4$ ), 6.98–7.632 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.66 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{23}\text{H}_{21}\text{N}_7\text{O}_3$   $[\text{M}]^+$  443.17, found 443.47; Anal. calcd. C, 62.29; H, 4.77; N, 22.11; O, 10.82 Found: C, 62.41; H, 4.52; N, 21.86; O, 10.99 %  $^{13}\text{C}$  NMR, 13.3, 20.7, 28.4, 28.5, 35.9, 55.5, 57.1, 111.9, 112.5, 113.0, 114.5, 114.9, 119.1, 119.4, 132.2, 147.4, 151.3, 152.5, 154.8, 155.4, 158.3, 159.5, 198.2.

2-amino-7, 7-dimethyl-4-(3-methyl-1-phenyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4e)

White solid (1.589 g, 96%), mp 222 °C; IR (KBr):  $\nu$  = 3352, 3365, 2195, 1675, 1202  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.91 (3H), 1.01–2.32 (6H, m,  $3\times\text{CH}_2$ ), 4.21 (1H, s,  $\text{H}_4$ ), 7.49–8.26 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.85 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{24}\text{H}_{23}\text{N}_7\text{O}_2$   $[\text{M}]^+$  441.19, found 441.50; Anal. calcd. C, 65.29; H, 5.25; N, 22.21; O, 7.25; Found: C, 65.44; H, 5.58; N, 22.37; O, 7.05 %  $^{13}\text{C}$  NMR, 13.2, 20.5, 27.1, 28.0, 32.2, 38.3, 50.9, 57.8, 113.7, 118.6, 118.8, 119.3, 119.9, 126.5, 129.1, 129.6, 139.9, 147.8, 151.7, 152.4, 154.9, 155.6, 159.4, 197.9.

2-amino-4-(1-(4-chlorophenyl)-3-methyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-7, 7-dimethyl-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4f)

White solid (1.569 g, 94%), mp 218°C; IR (KBr):  $\nu$  = 3419, 3362, 2195, 1667, 1213  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.93 (3H), 1.12–2.30 (6H, m,  $3\times\text{CH}_2$ ), 4.26 (1H, s,  $\text{H}_4$ ), 7.31–

7.56 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.78 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{24}\text{H}_{22}\text{ClN}_7\text{O}_2$   $[\text{M}]^+$  475.15, found 475.94; Anal. calcd. C, 60.57; H, 4.66; Cl, 7.45; N, 20.60; O, 6.72; Found: C, 60.23; H, 4.73; Cl, 7.67; N, 20.21; O, 6.45%  $^{13}\text{C}$  NMR, 13.0, 27.4, 27.4, 28.2, 32.6, 38.7, 51.1, 58.0, 114.2, 119.0, 119.4, 119.7, 120.0, 129.1, 129.7, 131.9, 138.0, 146.8, 151.3, 152.5, 154.5, 155.3, 159.8, 198.4.

2-amino-7, 7-dimethyl-4-(3-methyl-1-(p-tolyl)-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4g)

White solid (1.489 g, 92%), mp 219 °C; IR (KBr):  $\nu$  3444, 3317, 2196, 1642, 1254  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.93 (3H), 1.81–2.78 (6H, m,  $3\times\text{CH}_2$ ), 4.31 (1H, s,  $\text{H}_4$ ), 7.27–7.57 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.91 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{25}\text{H}_{25}\text{N}_7\text{O}_2$   $[\text{M}]^+$  455.21, found 455.52; Anal. calcd. C, 65.92; H, 5.53; N, 21.52; O, 7.02; Found: C, 66.17; H, 5.76; N, 21.79; O, 7.56%  $^{13}\text{C}$  NMR, 13.5, 21.5, 27.9, 26.7, 28.2, 32.5, 38.8, 51.7, 58.3, 113.5, 119.3, 119.6, 124.9, 125.3, 129.5, 129.9, 135.5, 136.5, 147.6, 151.9, 152.3, 154.6, 155.5, 159.7, 198.7.

2-amino-4-(1-(4-methoxyphenyl)-3-methyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-7, 7-dimethyl-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (4h)

White solid (1.509 g, 95%), mp 220 °C; IR (KBr):  $\nu$  3449, 3373, 2203, 1672, 1214  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.94 (3H), 1.81–2.50 (6H, m,  $3\times\text{CH}_2$ ), 4.23 (1H, s,  $\text{H}_4$ ), 7.31–7.66 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.91 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{25}\text{H}_{25}\text{N}_7\text{O}_3$   $[\text{M}]^+$  471.20, found 471.52; Anal. calcd. C, 63.68; H, 5.34; N, 20.79; O, 10.18; Found: C, 63.99; H, 5.03; N, 20.47; O, 10.58%  $^{13}\text{C}$  NMR, 13.4, 27.1, 27.3, 28.2, 32.3, 38.7, 51.2, 54.9, 58.7, 112.6, 112.9, 113.5, 114.7, 115.0, 118.9, 119.3, 132.2, 147.5, 151.2, 152.6, 154.4, 155.2, 158.5, 159.6, 199.2.

2-amino-7-methyl-4-(3-methyl-1-phenyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-4H, 5H-pyrano [4, 3-b] pyran-3-carbonitrile (4i)

White solid (1.250 g, 91%), mp 221 °C; IR (KBr):  $\nu$  = 3416, 3364, 2195, 1673, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.91 (3H), 2.21–6.42 (6H, m,  $4\times\text{CH}_2$ ), 4.41 (1H, s,  $\text{H}_4$ ), 7.25–8.56 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.82 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_7\text{O}_3$   $[\text{M}]^+$  427.14, found 427.42; Anal. calcd. C, 61.82; H, 4.01; N, 22.94; O, 11.23; Found: C, 61.91; H, 3.88; N, 23.08; O, 11.51%  $^{13}\text{C}$  NMR, 12.9, 21.1, 29.8, 58.1, 100.3, 100.5, 118.3, 118.9, 119.2, 119.4, 126.4, 129.2, 129.8, 139.1, 147.1, 151.1, 152.2, 154.5, 158.9, 162.1, 163.2, 175.5.

2-amino-4-(1-(4-chlorophenyl)-3-methyl-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-7-methyl-5-oxo-4H, 5H-pyrano [4, 3-b] pyran-3-carbonitrile (4j)

White solid (1.189 g, 89%), mp 219 °C; IR (KBr):  $\nu$  = 3419, 3335, 2194, 1673, 1249  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.91 (3H), 2.32–6.23 (6H, m,  $4\times\text{CH}_2$ ), 4.43 (1H, s,  $\text{H}_4$ ), 7.34–7.56 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.67 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{22}\text{H}_{16}\text{ClN}_7\text{O}_3$   $[\text{M}]^+$  461.10, found 461.87; Anal. calcd. C, 57.21; H, 3.49; Cl, 7.68; N, 21.23; O, 10.39; Found: C, 56.78; H, 3.88; Cl, 7.23; N, 21.76; O, 10.01%  $^{13}\text{C}$  NMR, 12.7, 21.0, 30.1, 58.3, 100.6, 100.7, 119.1, 119.8, 119.9, 120.8, 129.1, 129.6, 131.4, 136.6, 146.1, 151.3, 152.2, 154.6, 158.2, 161.6, 163.2, 175.1.

2-amino-7-methyl-4-(3-methyl-1-(p-tolyl)-5-(1H-1, 2, 4-triazol-1-yl)-1H-pyrazol-4-yl)-5-oxo-4H, 5H-pyrano [4, 3-b] pyran-3-carbonitrile (4k)

White solid (1.289 g, 90%), mp 223 °C; IR (KBr):  $\nu$  = 3414, 3378, 2192, 1671, 1252  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.94 (3H) 2.43–6.43 (6H, m,  $4\times\text{CH}_2$ ), 4.21 (1H, s,  $\text{H}_4$ ), 7.27–7.58 (8H, m, Ar-H+ $\text{NH}_2$ ), 6.43 (1H, s, NH) ppm; MS calcd. for  $\text{C}_{23}\text{H}_{19}\text{N}_7\text{O}_3$   $[\text{M}]^+$  441.15, found 441.45; Anal. calcd. C, 62.58; H, 4.34; N, 22.21; O, 10.87; Found: C, 62.69; H, 3.67; N, 22.50; O,

11.21%  $^{13}\text{C}$  NMR, 12.9, 19.8, 21.4, 30.5, 58.7, 100.3, 100.8, 119.0, 119.8, 125.1, 125.8, 129.6, 129.9, 134.7, 136.2, 147.4, 151.2, 152.8, 154.2, 160.1, 162.2, 163.6, 174.5.

2-amino-4-(1-(4-methoxyphenyl)-3-methyl-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazol-4-yl)-7-methyl-5-oxo-4*H*, 5*H*-pyrano [4, 3-*b*] pyran-3-carbonitrile (4l)

White solid (1.342 g, 90%), mp 224 °C; IR (KBr): $\nu$  = 3375, 3385, 2192, 1665, 1252  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.93(3H)2.46-6.64 (8H, m,  $4\times\text{CH}_2$ ), 4.36 (1H, s,  $\text{H}_4$ ), 7.27-7.62(8H, m, Ar-H+ $\text{NH}_2$ ), 6.55(1H, s, NH) ppm; MS calcd. for  $\text{C}_{23}\text{H}_{19}\text{N}_7\text{O}_4$  [M] $^+$ 457.15, found457.45; Anal. calcd C, 60.39; H, 4.19; N, 21.43; O, 13.99; Found: C, 60.02; H, 4.53; N, 21.88; O, 13.25%  $^{13}\text{C}$  NMR, 12.8, 20.7, 28.5, 55.1, 58.2, 100.4, 101.2, 112.0, 112.2, 113.9, 114.5, 119.0, 119.4, 132.2, 147.4, 151.2, 152.5, 154.7, 158.1, 158.8, 160.2, 162.4, 172.3.

2-amino-4-(3-methyl-1-phenyl-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazol-4-yl)-5-oxo-4*H*, 5*H*-pyrano [3, 2-*c*] chromene-3-carbonitrile (4m)

White solid (1.328 g, 92%), mp 225 °C; IR (KBr): $\nu$  = 3416, 3356, 2195, 1673, 1241  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  =1.92(3H), 7.39-7.82 (8H, m,  $4\times\text{CH}_2$ ), 4.41 (1H, s,  $\text{H}_4$ ), 7.50-8.43(8H, m, Ar-H+ $\text{NH}_2$ ), 6.91(1H, s, NH) ppm; MS calcd. for  $\text{C}_{25}\text{H}_{17}\text{N}_7\text{O}_3$  [M] $^+$ 463.14, found463.46; Anal. calcd. C, 64.79; H, 3.70; N, 21.16; O, 10.36; Found: C, 64.21; H, 3.69; N, 21.35; O, 10.56%  $^{13}\text{C}$  NMR, 12.9, 29.4, 57.7, 104.6, 115.3, 116.8, 118.8, 119.1, 119.5, 119.9, 123.3, 125.5, 126.6, 128.1, 129.2, 129.6, 139.1, 147.6, 151.2, 152.3, 153.2, 154.7, 159.2, 160.4, 162.3.

2-amino-4-(1-(4-chlorophenyl)-3-methyl-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazol-4-yl)-5-oxo-4*H*, 5*H*-pyrano [3, 2-*c*] chromene-3-carbonitrile (4n)

White solid (1.502 g, 93%), mp 220 °C; IR (KBr): $\nu$  = 3426, 3366, 2195, 1673, 1249  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  =1.94(3H), 7.38-7.82 (8H, m,  $4\times\text{CH}_2$ ), 4.43 (1H, s,  $\text{H}_4$ ), 7.53-7.52(8H, m, Ar-H+ $\text{NH}_2$ ), 6.92(1H, s, NH) ppm; MS calcd. for  $\text{C}_{25}\text{H}_{16}\text{ClN}_7\text{O}_3$  [M] $^+$ 497.10, found 497.90; Anal. calcd. C, 60.31; H, 3.24; Cl, 7.12; N, 19.69; O, 9.64; Found: C, 60.63; H, 3.09; Cl, 6.69; N, 19.04; O, 9.14%  $^{13}\text{C}$  NMR, 13.1, 29.2, 58.0, 104.2, 115.8, 116.5, 118.3, 119.1, 119.5, 119.8, 122.7, 125.4, 127.2, 129.1, 29.4, 131.4, 137.3, 147.2, 150.7, 152.5, 152.8, 154.2, 158.2, 160.1, 162.3.

2-amino-4-(3-methyl-1-(*p*-tolyl)-5-(1*H*-1,2, 4-triazol-1-yl)-1*H*-pyrazol-4-yl)-5-oxo-4*H*, 5*H*-pyrano [3, 2-*c*] chromene-3-carbonitrile (4o)

White solid (1.677 g, 95%), mp 219 °C; IR (KBr): $\nu$  = 3391, 3313, 2193, 1665, 1256  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.93(3H)7.41-7.86 (8H, m,  $4\times\text{CH}_2$ ), 4.29 (1H, s,  $\text{H}_4$ ), 7.14-7.56(8H, m, Ar-H+ $\text{NH}_2$ ), 6.95(1H, s, NH) ppm; MS calcd. for  $\text{C}_{26}\text{H}_{19}\text{N}_7\text{O}_3$  [M] $^+$  477.15, found477.48; Anal. calcd. C, 65.40; H, 4.01; N, 20.53; O, 10.05; Found: C, 66.77; H, 4.45; N, 20.56; O, 10.54%  $^{13}\text{C}$  NMR 13.1, 21.7, 29.1, 57.9, 105.5, 115.0, 116.2, 119.0, 119.5, 123.3, 125.1, 125.3, 126.1, 128.3, 129.2, 129.8, 135.2, 136.1, 147.0, 151.2, 152.1, 152.5, 154.2, 159.5, 160.3, 161.4.

2-amino-4-(1-(4-methoxyphenyl)-3-methyl-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazol-4-yl)-5-oxo-4*H*, 5*H*-pyrano [3, 2-*c*] chromene-3-carbonitrile (4p)

White solid (1.803 g, 97%), mp 223 °C; IR (KBr): $\nu$  =3392, 3318, 2193, 1664, 1253  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 1.90(3H)7.42-7.77 (8H, m,  $4\times\text{CH}_2$ ), 4.42 (1H, s,  $\text{H}_4$ ), 6.85-7.60(8H, m, Ar-H+ $\text{NH}_2$ ), 6.98(1H, s, NH) ppm; MS calcd. for  $\text{C}_{26}\text{H}_{19}\text{N}_7\text{O}_4$  [M] $^+$  493.15, found493.48; Anal. calcd C, 63.28; H, 3.88; N, 19.87; O, 12.97; Found: C, 62.65; H, 4.11; N, 20.22; O, 12.54%  $^{13}\text{C}$  NMR, 13.4, 29.4, 55.5, 58.5, 105.2, 112.1, 112.2, 114.9, 115.0, 115.2, 116.6, 119.5, 119.7, 123.1, 125.1, 127.9, 132.3, 147.4, 151.2, 152.1, 152.5, 154.1, 158.4, 159.1, 160.6, 161.5.

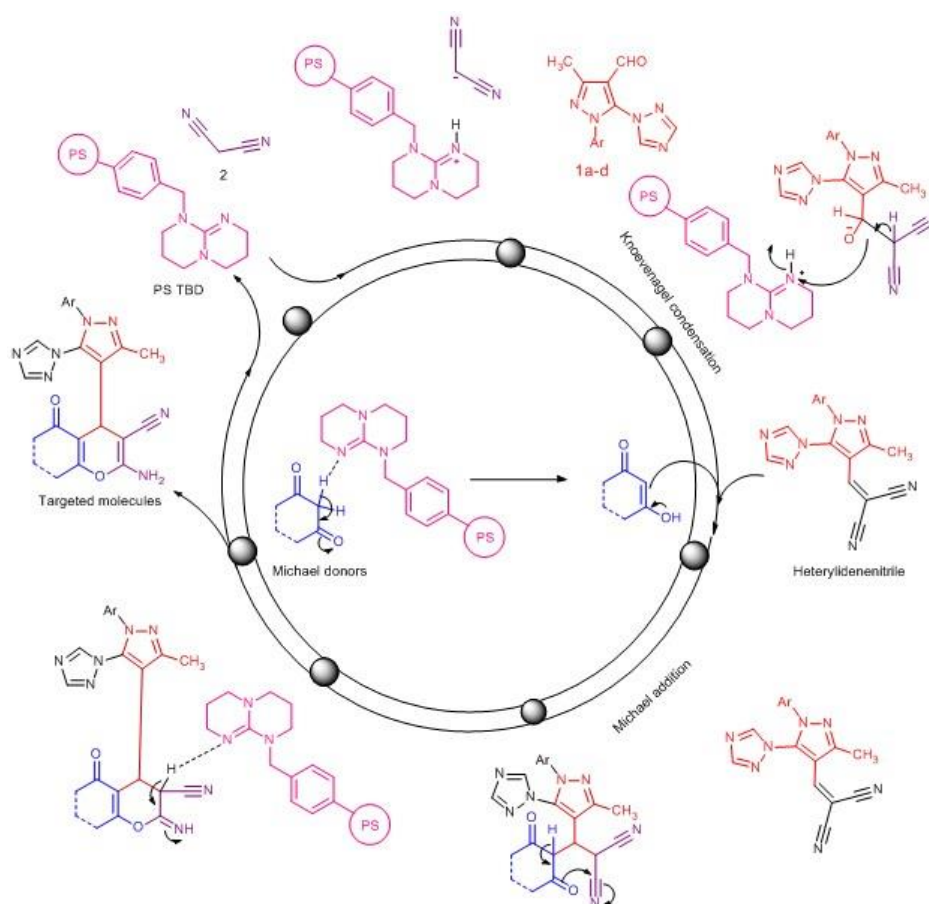
### 3. RESULTS AND DISCUSSION

#### 3.1. Chemistry

A series of 16 compounds, 4*H*-chromene **4a-d** and **4e-h**, pyrano[4, 3-*b*]pyran **4i-l** and pyrano[3, 2-*c*]chromene **4m-p** were synthesized by the plausible reaction mechanism depicted in Scheme 2. The reaction was optimized by varying temperature, time and amount of catalyst (Table 1). We found that reaction of 3-methyl-1-(4-substituted phenyl)-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazole-4-carbaldehyde **1a-d**, malononitrile (**2a**) and 4-hydroxy-coumarin (**3d**) with 5 mol% PS-TBD, in ethanol at 80°C for 1.5 h gave 95% yield of **4a**. Further increasing loading of catalyst didn't impact on yield. The catalytic activity of PS-TBD was investigated and it was found that PS-TBD maintained its efficiency up to five runs (Table 2). The newly synthesized compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR and elemental analysis. The molecular weight of compounds was confirmed by mass spectrometry. Physical, analytical and spectroscopic characterization data of all compounds are given in Supplementary material.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ) spectrum of **4a** exhibited a singlet peak around 4.23 ppm stands for  $\text{H}_4$  proton. Amine and aromatic protons of **4a** resonate as multiplets at around 7.58–8.54 ppm.  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ) spectrum shows characteristic peak at 28.6 ppm for cyclized carbon, 58.3 ppm for C–CN, 119.3 ppm for C $\equiv$ N, 152.4 ppm for C– $\text{NH}_2$  and 159.5 ppm for C=O, all these peaks support the structure of **4a**. The IR spectrum of compound **4a** exhibited characteristic absorption bands around 3428–3344  $\text{cm}^{-1}$  and 2189  $\text{cm}^{-1}$  stands for (asym. & sym. stretching) – $\text{NH}_2$  and –CN functional groups, respectively. The characteristic absorption band of C=O stretching and C–O–C ether stretching are observed around 1677  $\text{cm}^{-1}$  and 1241  $\text{cm}^{-1}$ .

The plausible reaction mechanism can be discussed as, in the first step, heterylidenenitrile forms by the Knoevenagel condensation of 3-methyl-1-(4-substituted phenyl)-5-(1*H*-1, 2, 4-triazol-1-yl)-1*H*-pyrazole-4-carbaldehyde (**4a-d**) and pre-activated malononitrile **2a** in the presence of PS-TBD. The catalyst PS-TBD abstracts the acidic proton of malononitrile and makes it more nucleophilic towards a facial attack on the carbonyl carbon of aldehyde. In second step, Michael addition of activated (**3a-d**) on heterylidenenitrile results into targeted molecules (**4a-p**). The catalyst is used in another cycle for synthesis of targeted molecules.





[Scheme 3]

#### 4. CONCLUSION

In summary, use of PS-TBD as a reusable catalyst is proved to be very effective for the synthesis of titled compounds. 5 mol% PS-TBD showed good catalytic activity up to five runs with good yield of desired products in less time, that reduce economical cost and environmental pollution.

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